

Corrosion Considerations for Thermochemical Biomass Liquefaction Process Systems in Biofuel Production

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Thermochemical liquefaction processing of biomass to produce bio-derived fuels (e.g., gasoline, jet fuel, diesel, home heating oil, etc.) is of great recent interest as a renewable energy source. Approaches under investigation include direct liquefaction, hydrothermal liquefaction, hydrolysis, fast pyrolysis, etc., to produce energy dense liquids that can be utilized as produced or further processed to provide products of higher value. An issue with bio-oils is that they tend to contain significant concentrations of organic oxygenates, including acids, which make the bio-oil a potential source of corrosion issues in transport, storage, and use. Efforts devoted to modified/further processing of bio-oils to make them less corrosive are currently being widely pursued. Another issue that must also be addressed in bio-oil liquefaction is potential corrosion issues in the process equipment. Depending on the specific process, bio-oil liquefaction production temperatures are typically in the 300–600°C range, and the process environment can contain aggressive sulfur and halide species from both the biomass used and/or process additives. Detailed knowledge of the corrosion resistance of candidate process equipment alloys in these bio-oil production environments is currently lacking. This paper summarizes recent, ongoing efforts to assess the extent of corrosion of bio-oil process equipment, with the ultimate goal of providing a basis for the selection of the lowest cost alloy grades capable of providing the long-term corrosion resistance needed for future bio-oil production plants.

INTRODUCTION

Biomass as a sustainable, renewable energy source is of increasing interest world-wide, with both biochemical and thermochemical conversion approaches being pursued. In addition to direct combustion of biomass for energy production, e.g., biomass-fired boilers [e.g., Refs. 1, 2], biomass can

be used to produce solid (by torrefaction), liquid (by liquefaction or pyrolysis), and gaseous (by pyrolysis or gasification) bio-derived fuels [e.g., Ref. 3]. Liquefaction thermochemical processing of biomass to produce liquid fuels such as gasoline, jet fuel, diesel, home heating oil, etc. is of particular recent interest,^{3–10} with a number of pilot scale and/or commercial start-ups in early operational stages.

A wide variety of non-food biomass feed stocks are currently being evaluated, including woody species, grasses, algae, and agricultural residue. Process temperatures in the initial deconstruction of the biomass by pyrolysis or liquefaction approaches (with or without catalysts) are typically in the 300–600°C range. The biomass deconstruction yields vapor/liquid/solid mixtures that can be condensed

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and separated to bio-oil products (Fig. 1).¹¹ The bio-oil products can then be upgraded by various hydrotreating, separation, and fractionation steps to the final desired fuel form (Fig. 1). Specific processes under investigation include direct liquefaction, hydrothermal liquefaction, hydropyrolysis, and fast pyrolysis.^{3–10} The fast pyrolysis methods

typically involve rapid heating of the biomass in the absence of oxygen to 500–600°C range, whereas liquefaction approaches use water or other solvents at lower temperatures than pyrolysis (less than approximately 400–450°C) but higher pressures.^{6–9} The major overall challenge is the economical production of high quality bio-oil fuels with costs comparable to fossil-derived fuels.

The initial resultant bio-oil products can contain high oxygen contents (up to ~30% to 50% range) and significant concentrations of organic oxygenates, including acids, which make the bio-oil a potential source of corrosion issues in transport, storage, and use.^{10,12–14} Of particular concern are carboxylic acids (formic, acetic, etc.), which make the bio-oils very corrosive to lower alloy steels and aluminum.^{14–25} Processing and upgrading approaches to reduce the acid content and corrosivity of bio-oils is an active area of research. However, a relatively understudied aspect is the potential for corrosion in the bio-oil process equipment.

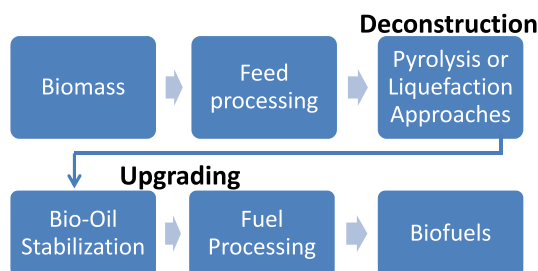


Fig. 1. Schematic overview of biomass pyrolysis/liquefaction route to biofuels (after Ref. 11).

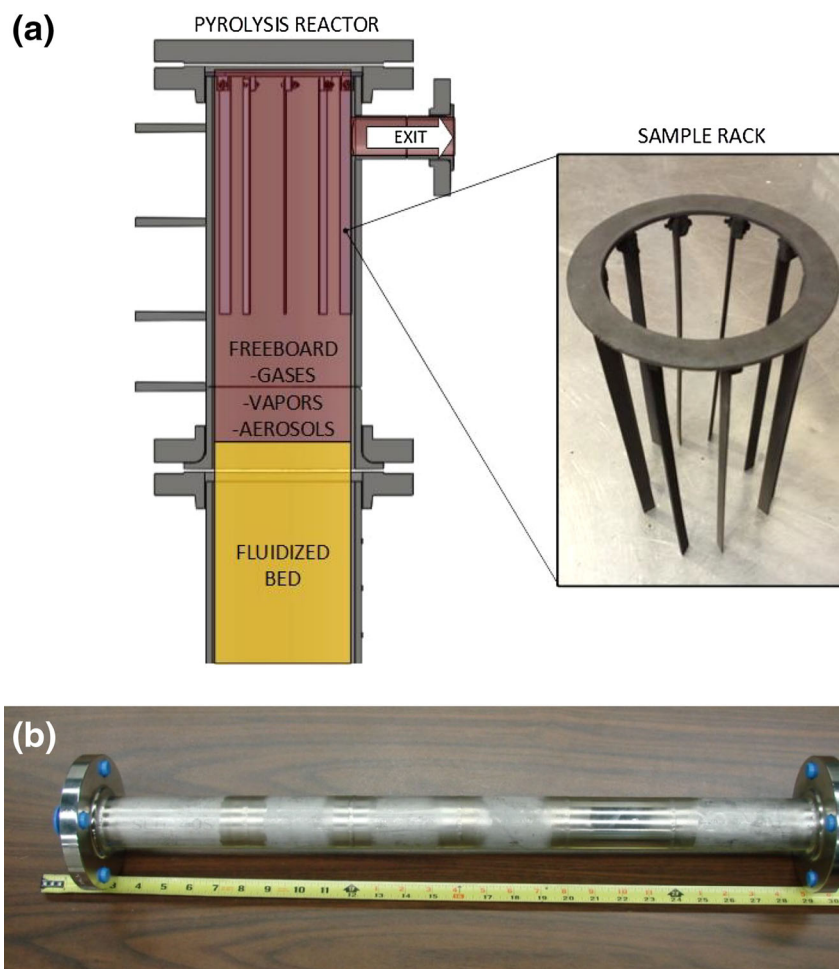


Fig. 2. Examples of exposure methods. (a) Test samples and holder for insertion in an operating liquefaction system in Iowa State University's Pyrolysis Process Development Facility.²⁹ The rectangular test coupons in this example were ~25 cm × 1.3 cm × 0.3 cm, with a ring holder outer diameter of 17 cm permitting exposure of 10 test samples. (b) Typical tube spool section composed of multiple alloys welded together for replacement of a liquefaction system tubing section. Image (b) from Ref. 27.

Table I. Nominal base compositions (wt.%) of select candidate alloys of interest for bio-oil liquefaction processing equipment (listed in approximate order of least to most expensive)

Alloy	Fe	Ni	Cr	Mo	Mn	Si	C	other
410	Balance		11.5–13.5			1.0 max	0.15 max	
201	Balance	3.5–5.5	16–18		5.5–7.5	1.0 max	0.15 max	0.25 N max
301	Balance	6–8	16–18		2 max	0.75 max	0.15 max	0.1 N max
304L	Balance	8–12	18–20		2 max	0.75 max	0.03 max	0.1 N max
316L	Balance	10–14	16–18	2–3	2 max	0.75 max	0.03 max	0.1 N max
317L	Balance	11–15	18–20	3–4	2 max	0.75 max	0.03 max	0.1 N max
310 ^a	Balance	19–22	24–26		2 max	1.5 max	0.25 max	–
904L	Balance	23–28	19–23	4–5	2 max	1.0 max	0.02 max	1–2 Cu
800 ^a	Balance	30–35	19–23		1.5 max	1 max	0.1 max	Al, Ti 0.15–0.6
825	Min 22	Balance	19.5–23.5	2.5–3.5	1 max	0.5 max	0.05 max	1.5–3 Cu, 0.6–1.2 Ti
600	6–10	Balance	14–17		1 max	0.5 max	0.15 max	

^aSeveral high temperature grade variations available

An important consideration for scale-up of biomass liquefaction to achieve economical commercial production of fuel is the cost and durability of the plant process equipment. Unlike biomass gasification, which typically operates at temperatures in excess of 600°C and can result in highly aggressive, high-temperature corrosion conditions,² frequently necessitating costly, highly alloyed high-Ni austenitic or Ni-base alloys, the intermediate temperatures (300–600°C) and typically less aggressive corrosion conditions of liquefaction processes permit consideration of less costly stainless steels and related alloys. Assessment and understanding of the modes and extent of corrosive attack that may be encountered in liquefaction processes are needed to guide proper selection of alloys to meet plant durability requirements at the lowest possible capital cost. Alloy selection is critical as alloy costs can vary up to ~2 to 10 times between conventional stainless steels, high-Ni austenitics, and Ni-base alloys (driven primarily by the high cost of Ni, and Mo). The goal of this paper is to summarize recent, ongoing efforts led by Oak Ridge National Laboratory (ORNL)^{25–28} to assess the extent to which corrosion of bio-oil liquefaction process equipment may be an issue.

EXPERIMENTAL APPROACH

Unlike evaluation of the corrosivity of the bio-oil products themselves, which can readily be accomplished in a laboratory setting by immersion and/or electrochemical approaches, corrosion studies of biomass thermochemical liquefaction process conditions are difficult to simulate in the laboratory. This is due to the elevated temperatures, high pressures (in some processes), catalysts/process additives, flow conditions, and biomass feedstock handling. Therefore, to better understand the extent and nature of corrosion attack in biomass liquefaction process equipment, ORNL is collaborating

with multiple university, national laboratory, and industry partners to perform analyses of field-exposed alloy components from bench-top, pilot-scale, and commercial-scale systems. Where system designs permit, in situ exposure of candidate alloy test samples and pipe/tube spool pieces containing multiple alloy grades welded together, are also being pursued (see examples shown in Fig. 2).^{25–28} Alloys under evaluation were selected among type 410 ferritic stainless steel, conventional type 300 series austenitic stainless steels of varying Ni, Cr, and Mo content (301, 304L, 316L, 317L, and 347), low-Ni, high Mn austenitics such as grades 201 and related alloys, higher-Ni austenitics (310, 800, 904L and related high Ni, Mo, Cr grades), and the Ni-base alloys 600 and 825 (Table I). Duplex stainless steels such as grade 2205 (Fe-22Cr-5Ni-3Mo base) were not considered due to susceptibility to embrittlement at temperatures above approximately 300°C,³⁰ which falls within the intermediate temperature operation range of many liquefaction processes.

Post-exposure corrosion assessment of exposed components and test samples involved initial non-destructive acoustic techniques to detect areas of tube wall thinning and dye penetrants for detection of local cracking. These techniques along with visual examination were used to select areas for cross-section metallographic examination. Given the potential for a significant corrosion role by water soluble species such as chlorides from the biomass/processing, sample preparation was done using non-aqueous polishing media. Characterization was pursued by light microscopy (LM), scanning electron microscopy (SEM) with qualitative energy dispersive x-ray analysis (EDS), and electron probe microanalysis (EPMA) using both energy dispersive and wavelength dispersive techniques to obtain qualitative and quantitative information on elements such as O, S, Cl, P, Na, etc., as well as the alloy element constituents.

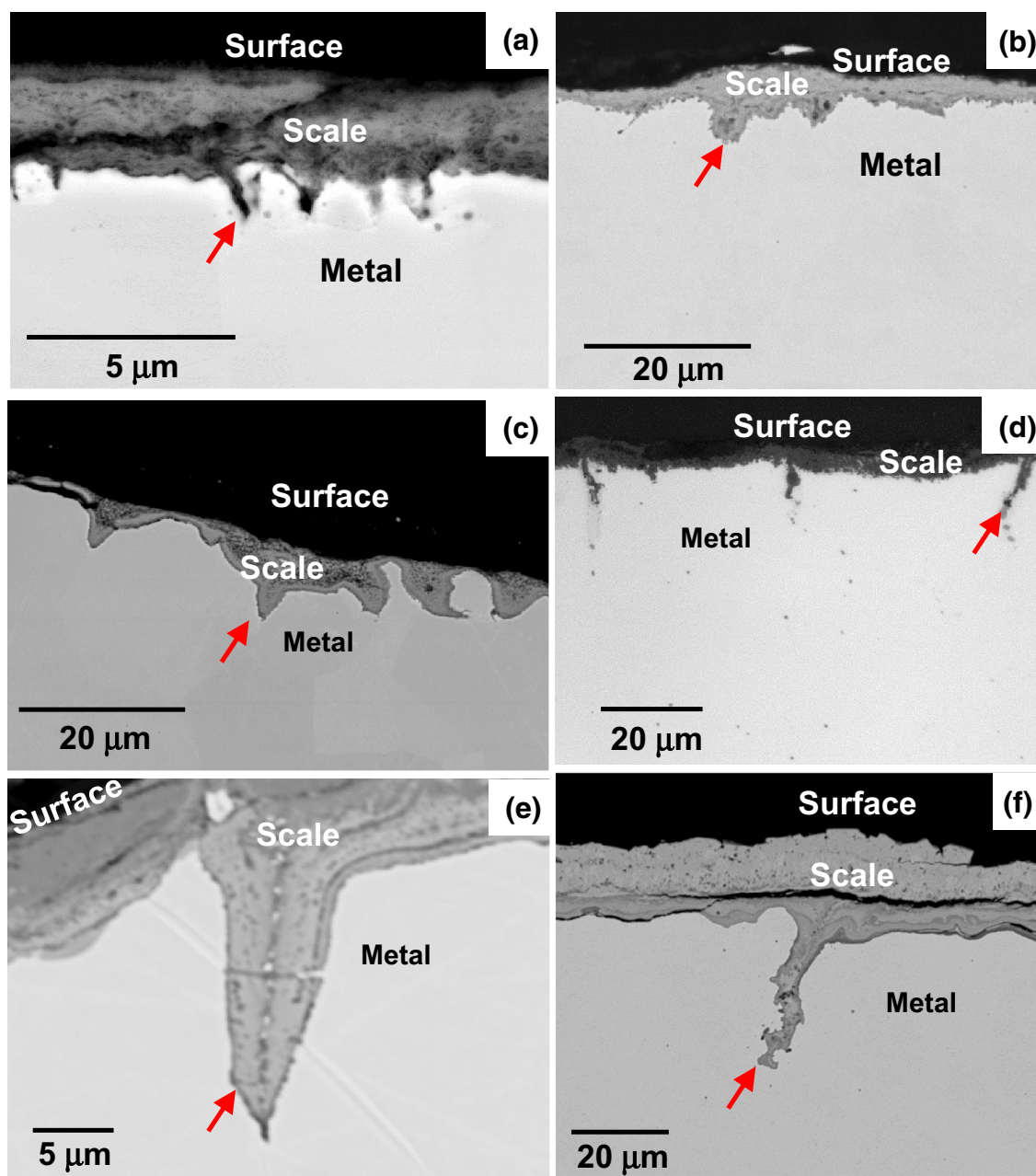


Fig. 3. Cross-section backscatter mode SEM (a–c, e, f) and LM (d) micrographs of type 316L (a–d, f) and 316H (e) stainless steel from a wide range of biomass liquefaction process system in situ test sample (a, b) and operated components (c–f) exposed at multiple locations. Preferential internal attack (arrows) is evident after relatively short operation, < 100–200 h for a, c; 600–1000 h range for b, d; and not available for e, f (likely < 1000 h). Image (c) after Ref. 26.

RESULTS AND DISCUSSION

Figure 3 shows an assemblage of SEM and LM cross-sections of type 316 (316L, low carbon, and 316H, high carbon for improved elevated temperature strength) stainless steel exposed in a wide range of biomass liquefaction process systems obtained from multiple collaborators (operation times on the order of ~100 to 1000 h). The specifics

of process approaches, additives, biomass sources, and operating conditions are considered proprietary in most cases. However, characterization findings for these type 316 stainless steels from multiple locations and liquefaction processes do suggest some common features. Oxide scaling was generally on the order of ~5 to 20 μm , suggesting relatively modest oxidation rates for these relatively short-term exposures. However, preferential internal

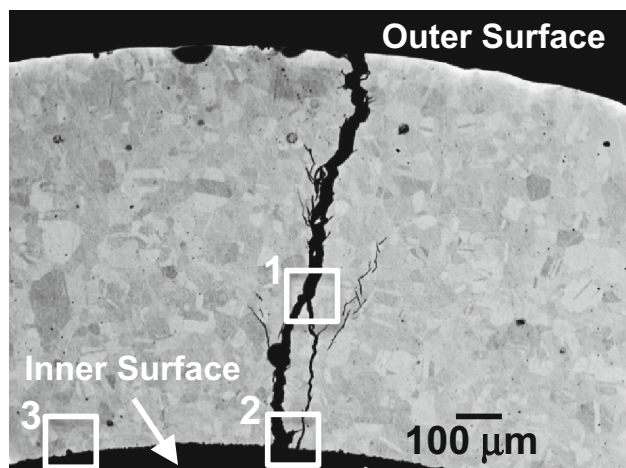


Fig. 4. Cross-section backscatter mode SEM image of a cracked 316L stainless steel tube from a biomass liquefaction process system.

attack (marked by arrows in Fig. 3) was also observed. Although not seen in all instances of field-exposed 316 stainless steel components and test samples examined to date by ORNL, such preferential internal attack has been observed in multiple settings. This attack has been observed both at alloy grain boundaries in some cases, and in intra-grain regions in other cases. The concern is that these features may continue to grow with time and act as stress concentrators that provide crack initiation sites over the course of the 10+ year lifetimes needed for commercial plant operation.

Cracking of components from operating systems after relative short exposure periods (<1000 h) has in fact been observed in several instances at multiple locations using different biomass liquefaction processes.^{25–28} These instances were related to off-normal operation conditions and/or out of specification catalysts and additives. An example is shown in Fig. 4 for a type 316L tube. Cracking proceeded through the entire wall thickness at several locations of the 6.4-mm outer diameter type 316L tube, appeared to be initiated at the tube inner surface, and was primarily transgranular in nature. Initial SEM EDS analysis suggested the cracking may have been associated with sulfur species. Based on this finding, detailed EPMA analysis was conducted within a cracked region, at the tube inner surface crack initiation site, and a nearby inner tube surface location without cracking, as shown in Figs. 5, 6, and 7, respectively.

Figure 5 shows a backscatter mode SEM image and EPMA maps at a cracked region within the tube wall thickness (Fig. 4, location 1). The maps indicate that the material in the crack is rich in Fe, O, S, Na, and Cl. At the inner tube surface crack region site (Fig. 6, location 2 in Fig. 4), products rich in O, S, Na, and Cl were again detected, along with P. The

intermediate temperature of liquefaction processes, including cyclic excursions to room temperature during downtimes, straddles the boundary between typically lower-temperature phenomenon such as stress corrosion cracking and higher temperature corrosion and cracking modes, complicating definitive identification of the specific mechanism(s) of cracking attack. Figure 7 shows the scale at the inner tube surface in a region without cracking (Fig. 4, location 3). Preferential internal attack (marked by arrows in Fig. 7a), qualitatively similar to those shown in Fig. 3, were evident and lend credence to the speculated possibility that such intrusions may be precursors to or eventually lead to cracking under some operating conditions.

EPMA mapping of the scale in this preferential internal attack region (Fig. 7) shows it to be O- and S-rich, with the internal protrusions also enriched in Cr and Mo and the outer scale regions more enriched in Fe. The presence of Cl, Na, and P was also detected, although they do not appear to be extensively enriched in the tip regions of the internal attack at the scale–alloy interface. Chlorine and sulfur species in particular are well established as potentially highly corrosive species encountered in biomass-fired boilers, although other species (N, P, K, Ca, Mg, Na, Si) are also frequently encountered and can be detrimental to corrosion resistance.^{2,31} The detection of S, Na, Cl, and P in components and test samples exposed to thermochemical biomass liquefaction system environments, and their possible association with enhanced corrosion attack and/or cracking, is therefore not surprising. Such species can be released from processing of the biomass itself, or potentially be introduced by process additives such as catalysts.

Exposure of a range of alloys in thermochemical biomass liquefaction system environments at multiple locations is currently in progress to better understand the mechanisms of attack and provide a basis to guide alloy selection. Figure 8 shows cross-section backscatter mode SEM images for initial exposures conducted at Iowa State University's Pyrolysis Process Development Facility (PPDF)²⁹ using the test sample design and location shown in Fig. 2a. The test alloy set consisted of ferritic type 410 stainless steel (Fe-11.5-13.5Cr wt.%), and austenitic stainless steels type 201 (3.5-5.5Ni, 16-18Cr, 5.5-7.5Mn), type 301 (6-8Ni, 16-18Cr), type 304L (8-12Ni, 18-20Cr), type 316L (10-14Ni, 16-18Cr, 2-3Mo), and type 317L (11-15Ni, 18-20Cr, 3-4Mo). These alloys were selected to represent a range of cost and potential corrosion resistance. The test coupons were successfully exposed to pyrolysis gas products in situ in the liquefaction system (Fig. 2a) operated with red oak and corn stover biomass for approximately 83 h of total operation at ~500°C (123 h including heating/cooling times).

Preliminary analysis (Fig. 8) indicated that the primary mode of attack was oxide scaling, with little internal attack and no cracking of the underlying

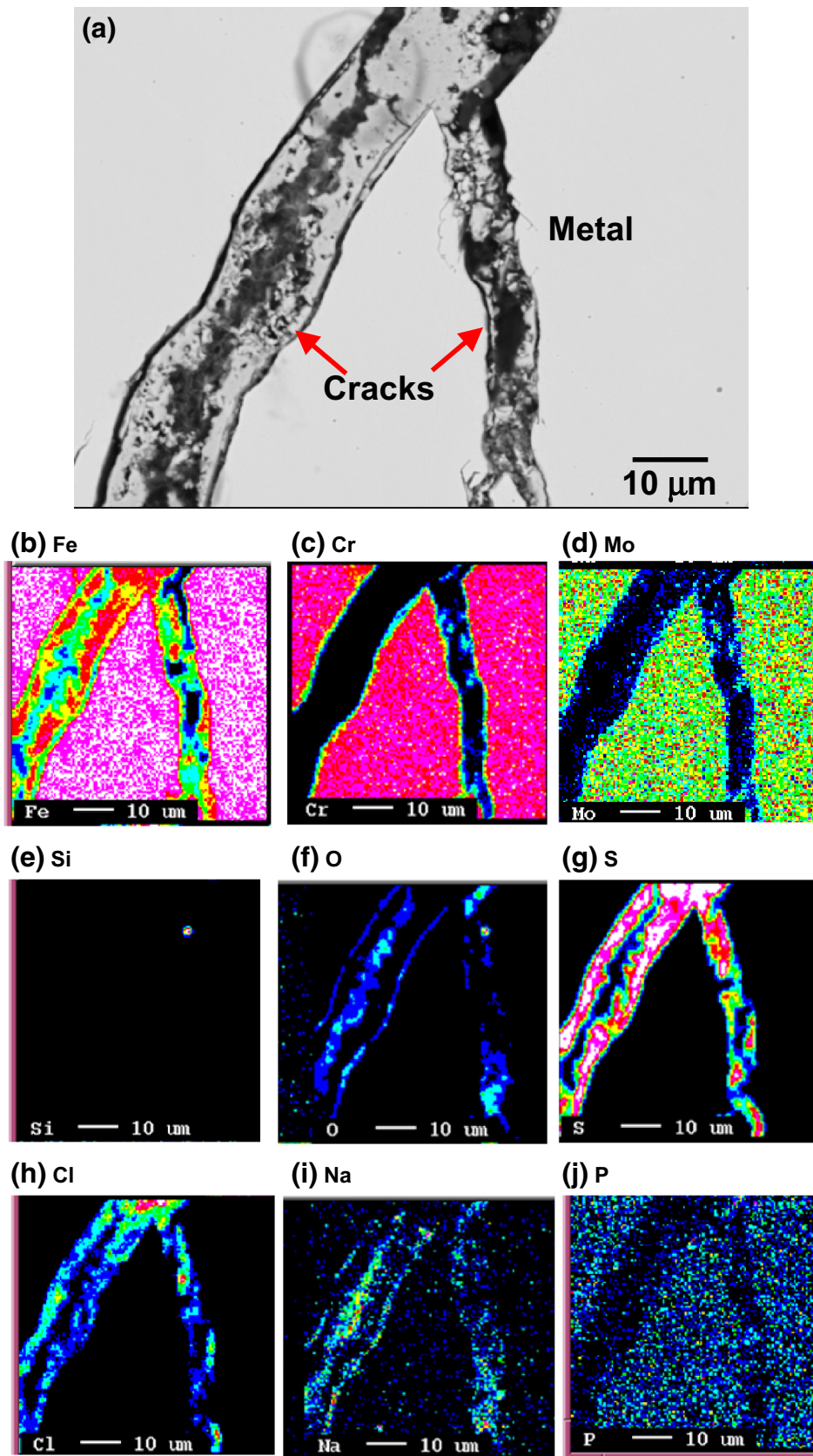


Fig. 5. EPMA analysis of location 1 (crack region) in Fig. 4 of the cracked 316L stainless steel tube from a biomass liquefaction process system. (a) Cross-section backscatter mode SEM image of mapped region; (b)–(j) Elemental maps: relative intensity increases from black (low) to blue to green to yellow to red to white (high).

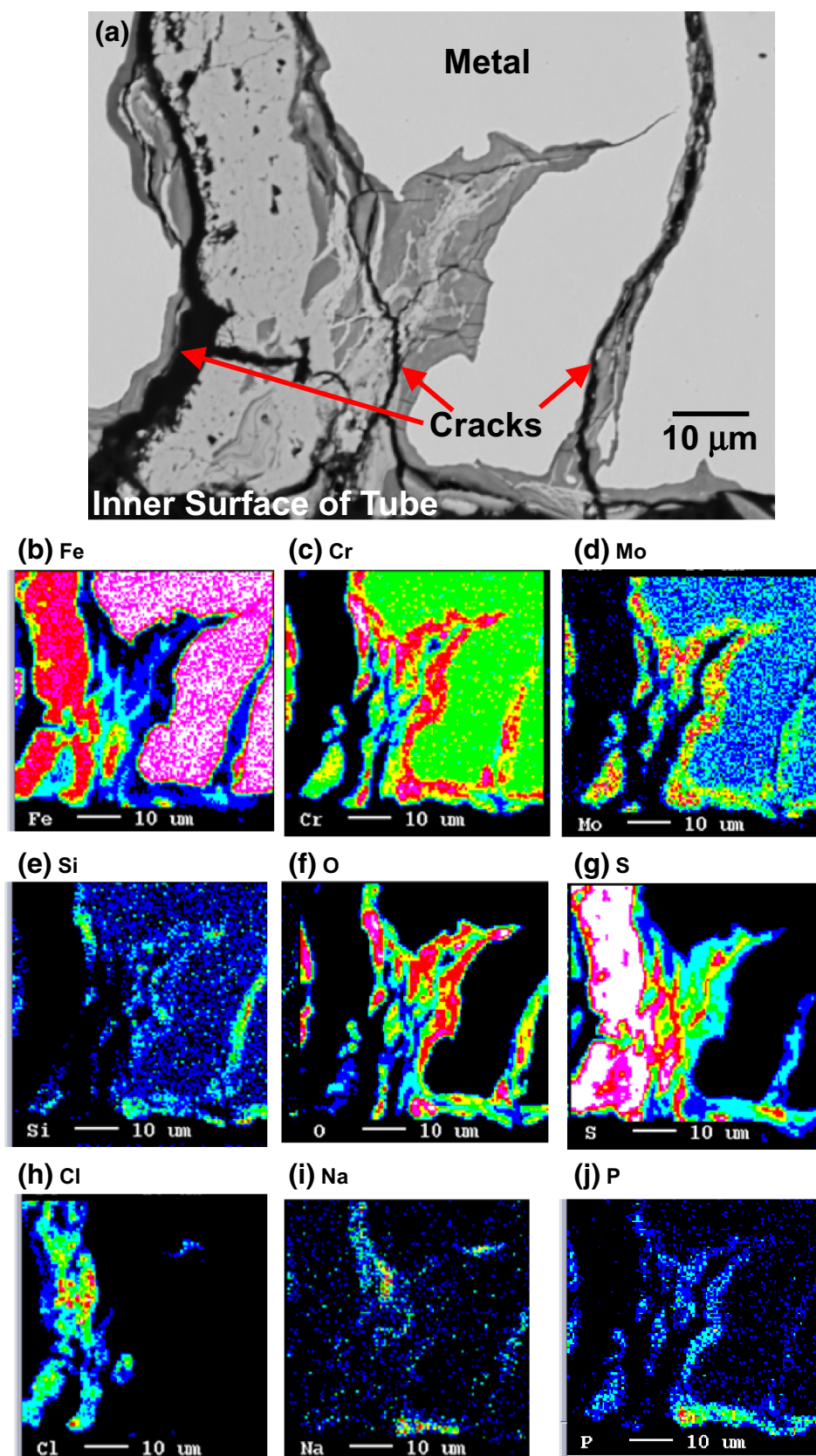


Fig. 6. EPMA analysis of location 2 (inner surface of tube) in Fig. 4 of the cracked 316L stainless steel tube from a biomass liquefaction process system. (a) Cross-section backscatter mode SEM image of mapped region; (b)–(j) Elemental maps: relative intensity increases from black (low) to blue to green to yellow to red to white (high).

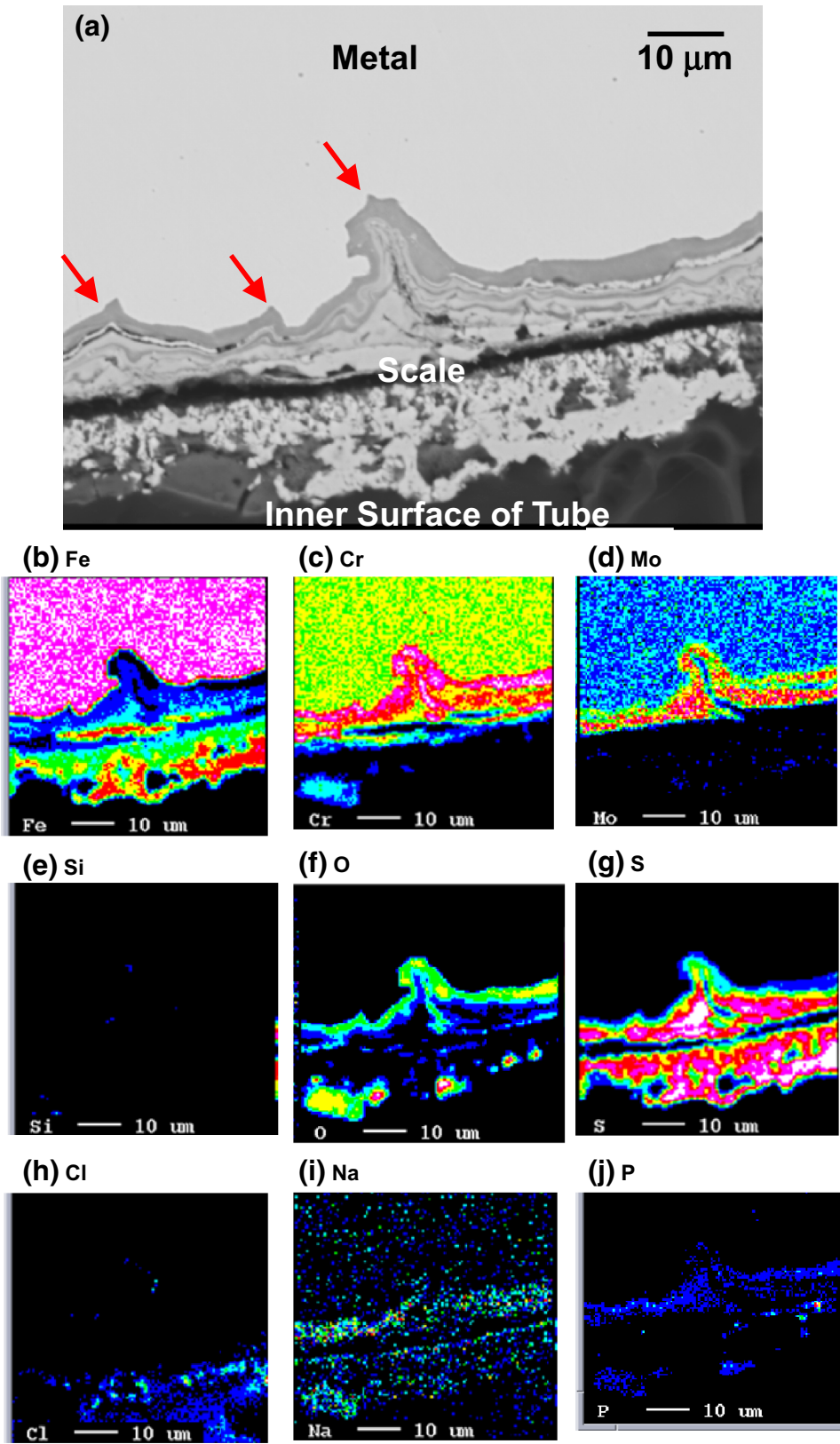


Fig. 7. EPMA analysis of location 3 (inner surface of tube away from cracks) in Fig. 4 of the cracked 316L stainless steel tube from a biomass liquefaction process system. (a) Cross-section backscatter mode SEM image of mapped region; (b)–(j) Elemental maps: relative intensity increases from black (low) to blue to green to yellow to red to white (high).

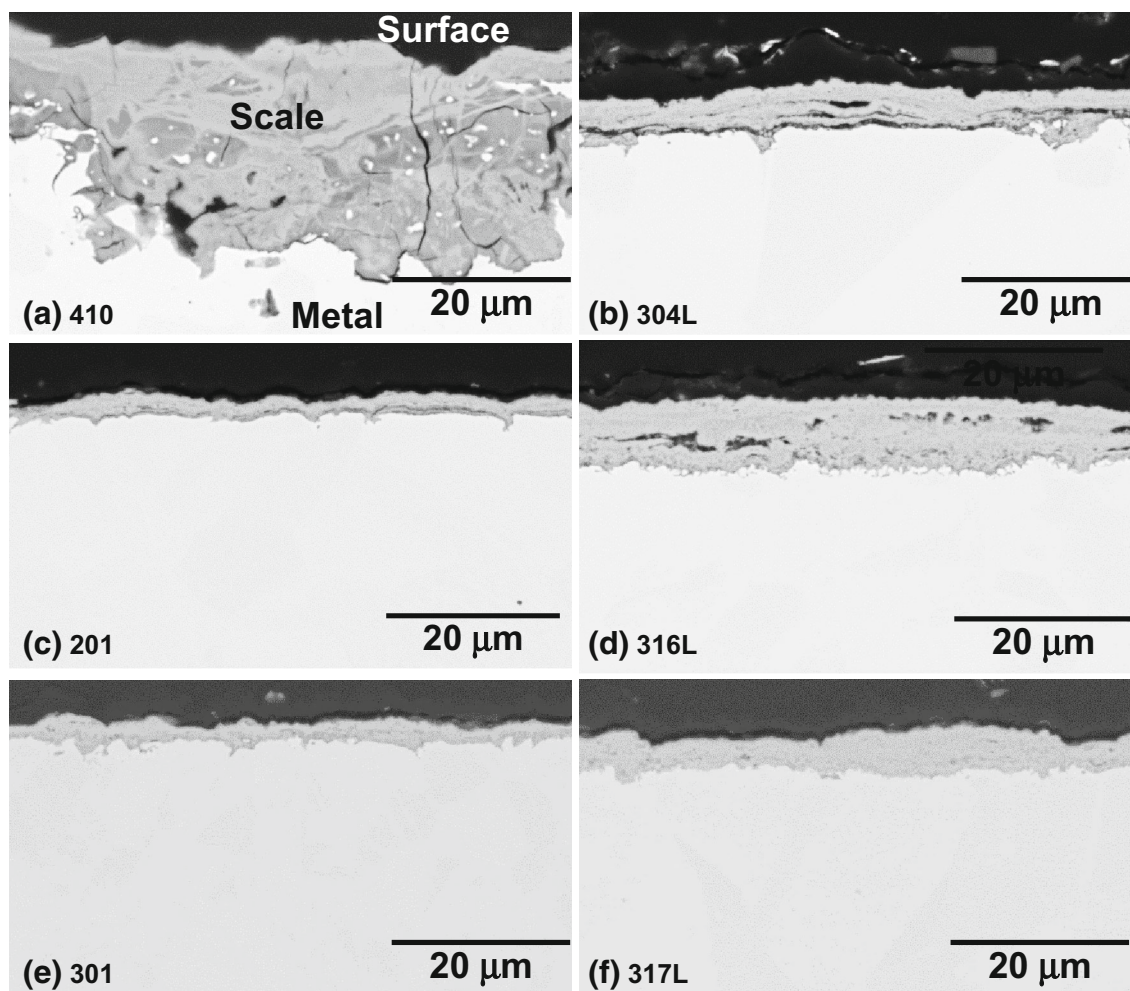


Fig. 8. SEM backscatter mode cross-section images of alloys after 83 operating hours (123 h total including heat up/cool down) at 500°C exposed to pyrolysis gas in the Iowa State pyrolysis facility.

alloy evident. In general, all the resulting scales consisted primarily of Fe-Cr-Si-rich oxide(s). However, small quantities of Na, K, Cl, and Ca were also detected by EDS surveying in some scale regions. Although not conclusive due to peak overlap issues, the EDS data also suggested that the scales may have contained some S (this issue will be further studied by EPMA). The greatest extent of scale formation was observed for type 410 stainless steel, the lowest Cr-containing alloy evaluated. Despite their relatively low cost, both types 201 and 301 showed (qualitatively) comparable to moderately less scaling than the more costly types 304L and 316L stainless steels in this initial exposure (Fig. 8). Duplicate alloy test samples are currently being exposed for longer times in the PPDF. Planned work includes characterization of scale formation and features as a function of exposure time, as well as metal thickness loss measurements after multiple exposure times to better quantify the kinetics and relative extent of corrosion among the alloy candidates.

CONCLUDING REMARKS

Characterization of both components from operating systems and alloy test sample exposures from a wide range of biomass thermochemical liquefaction process systems was pursued. Under a range of liquefaction processes, conventional type 316 stainless steels exhibited a tendency for preferential internal attack, which may lead to cracking under some circumstances. Corrosion and cracking appeared to be related to S, Na, and Cl species, in particular. Emphasis is therefore being placed on (1) obtaining alloys exposed for multiple and long time periods in the same setting to establish if the internal attack features grow with time and/or act as crack initiation sites, and (2) exposure of other grades of stainless steels and related alloys to guide future alloy selection. If Cl-related attack is a major issue, moving to higher alloy Ni, Cr and Mo contents (e.g., grade 317L and higher Ni, Mo austenitics such as 800 or 904L and/or Ni-base alloys) may prove helpful to reduce susceptibility to corrosion. How-

ever, if attack by S is a major issue, then moving to more costly high-Ni alloys may not be the answer, as high Ni levels are associated with susceptibility to sulfidation attack.^{26,27,32} In this regard, lower Ni, high Mn and Cr austenitics such as grade 201 may prove to be viable candidates.

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